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(54) A PROCESS FOR HYDROPHOBISING FINELY DIVIDED OXIDES

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany of 9 Weissfrauenstrasse, Frankfurt/Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for hydrophobising finely divided oxides.

The invention relates to a process for hydrophobising finely divided oxides of metals and/or of silicon by anchoring hydrocarbon radicals in firm chemical linkage to the oxide surface by treating the oxides with a hydrolysable metal or metalloid compound containing OR-groups.

It is known that oxides of metals or metalloids, for example of silicon, can be given hydrophobic properties by chemical reactions at the surface, for example by means of organochlorosilanes.

Products of this kind are distinguished by the fact that hydrocarbon radicals (preferably methyl) are anchored in firm chemical linkage to the surface of the finely divided oxides, with the result that they are provided with partial or complete permanent hydrophobicity, depending upon the quantity of hydrocarbon radicals present.

This method of hydrophobising is characterised by the fact that, at a certain "degree of hydrophobicity", the transition from completely hydrophilic to completely hydrophobic behaviour takes place more or less directly without any pronounced intermediate phase. For example, products of this kind containing e.g. 0.3% of C or less have hydrophilic properties and, in terms of application, behave in almost the same way as the starting materials, whilst corresponding products containing at least approximately 0.5 to 0.7% of C are almost completely hydrophobic at a carbon content which depends on the specific surface of the starting oxide. In terms of

application, corresponding products with an intermediate degree of hydrophobicity behave in the same way as mixtures of hydrophobic and hydrophilic oxides, and experience has shown that it is not possible in this way to obtain products which, although hydrophobic, i.e. cannot be wetted with water, have nevertheless retained a residue of hydrophilic affinity.

However, for certain applications, for example for thickening silicone rubber and other elastomers, it is desirable to have fillers which, although hydrophobic and hence decidedly organophilic, nevertheless show proton affinity as well.

The aforementioned hydrophobic products are unable to show this latter property because the alkyl or aryl radicals attached for example to silicon atoms do not show any proton affinity and the small residue of for example silane groups which is left in them (in the event of true chemical hydrophobising) is masked by the alkyl groups for example adjacent to them in large numbers in such a way that they can no longer have any affinity for protons. This latter effect is ultimately characteristic of the quality of products of this kind.

Completely hydrophobic oxides which, although not wetted by water, nevertheless show proton affinity, can be obtained by treating for example finely divided silicon dioxide in such a way that only a proportion of its silanol groups present at the surface is converted into silicon alkyl groups, whilst the remainder are converted for example into silicon alkoxy groups.

Unlike the silicon alkyl group, the silicon alkoxy group shows a certain degree of proton affinity.

According to an earlier proposal, products of this kind can be obtained for example from SiO_2 by treatment with for example organoalkoxysilanes. The quantitative ratio of the Si-alkyl to the Si-alkoxy groups present at the surface is, for example, equal to or greater than 1.

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One of the requirements which has to be satisfied by fillers which, on the one hand, are intended to be distinctly lipophilic but which, on the other hand, are intended to show high proton affinity coupled with wettability by water, is that they should contain at their surface as many suitable groups with proton affinity, for example silicon alkoxy groups, as possible, but as few silanol groups as possible or better still none at all, the number of silicon alkyl groups for example being only of auxiliary importance or of no importance at all.

To obtain fillers such as these would necessitate the closing of a gap which has hitherto existed in terms of application technology, as briefly outlined above.

In one known process (DAS 1,048,889), silica aerogels can be given organophilic properties by coating them with organic silicates to form a surface film of a polymeric organic silicate. Regarded in more detail, these products show a degree of polymerisation in the surface film in excess of 25, and can be hydrophilic, partly hydrophobic, but not organophilic, or alternatively hydrophobic and organophilic.

Since the materials in question are not uniform hydrophobic materials, but instead hydrophilic particles i.e. particles which basically can be wetted with water, wrapped in an organic more or less water-repellent layer, considerable quantities of organic "wrapping material" are required. Thus, approximately 20% by weight of for example tetra-ethyl ortho-silicate are required even to obtain only partly hydrophobic products.

It is obvious that disproportionately large quantities are required to obtain completely hydrophobic products, for which reason the production of completely hydrophobic products is also stated as being impracticable in the aforementioned DAS.

The present invention provides a process for hydrophobising finely divided oxides of metals and/or of silicon by anchoring hydrocarbon radicals in firm chemical linkage to the oxide surface by treating the oxides with hydrolysable metal or metalloid compounds containing OR-groups, by means of which process it is readily possible to produce lipophilic fillers which, although completely unwettable by water, nevertheless show high proton affinity, the aforementioned properties being obtained by genuine topochemical reactions at the active surfaces of the starting materials.

According to the invention finely divided oxides of metals and/or silicon are hydrophobised by anchoring hydrocarbon radicals in firm chemical linkage to the oxide surface by intensively mixing with the oxide a hydrolysable metal or metalloid compound containing —OR groups of the general formula

in which M represents an element of the IVth group of the Periodic System, especially titanium or silicon, whilst each R represents an alkyl radical with 1 to 8 carbon atoms or an aryl radical, it being possible for the radicals R in the same molecule to be the same or different, or with an oligomer of such a compound, the oxide having a water content of less than 1% by weight.

The ester compounds can be allowed to act through admixture upon the oxides at pressures in the range from 1,000 Torr to 10^{-3} Torr and at temperatures of from 20°C to 300°C over a period of from one minute to 24 hours, dry NH_3 -gas optionally being added to accelerate the reaction either before, during or after treatment of the oxide particles with the hydrolysable compound.

It is also possible to do without the treatment with NH_3 gas, although this does mean that the contact time has to be considerably lengthened until products which are completely unwettable by water are obtained.

The process according to the invention is applicable not only to pure metal oxides but also to oxide mixtures and mixed oxides. Preferably the oxide used as starting material has a water content of from 0.2% to 0%.

In the case of silicas or mixtures thereof with other metal oxides, for example Al_2O_3 or TiO_2 with a water content, emanating from storage or from the production process, of 1% by weight or more or without previous activation of the finely divided oxides which can be carried out by the process disclosed in British Patent Specification No. 1292328 or in British Patent Specification No. 1337329, the end products show either no hydrophobic properties or, where increased quantities of hydrophobising agents are used, only inadequate hydrophobic properties for otherwise the same treatment.

It is possible to use any ester compounds corresponding to the above general formula, although it is generally preferred to use those of the kind which, at the mixing temperatures envisaged, are gaseous or sufficiently volatile to be uniformly distributed upon contact with the moved oxide particles.

On the other hand, it is also possible to use less volatile ester compounds in liquid form which are best sprayed onto the oxide particles suitably offered or presented to them by methods known per se.

In one preferred embodiment, the ester compounds used are of the kind which, following admixture with the oxide particles pretreated in the manner described above, lead even at room temperature to products which are completely unwettable by water over periods of from 30 minutes to 3 hours.

Alkoxy or aryloxy silanes and the corresponding compounds of titanium have proved

to be particularly suitable. Preferably the oxide is admixed with the ester compound at a temperature of from 20°C to 200°C, more preferably from 20°C to 35°C.

- 5 According to another embodiment of the process after activation by treatment at a temperature of from 700 to 1000°C for a period of less than 60 seconds with a gas stream inert to the oxide, either in a fluidised bed or with
10 a stream of the inert gas flowing in counter-current to the oxide, the oxide is treated with a tetra-alkoxy silane or with an oligomer thereof.

- 15 Large-scale working of the process can be carried out in almost any way, continuous production obviously being preferred. In the latter case, the activated silicas or other oxides are admixed with the aforementioned hydrophobising agent and, optionally, with NH₃,
20 in a fluidised bed by methods known *per se*. If, as will generally be the case, the alcohol formed during the reaction and NH₃, if any, are to be removed, the reaction mixture subsequently passes through a relatively short or
25 relatively long residence zone, depending on the considerations referred to above, in order finally to be treated in countercurrent with a stream of a gas inert to the oxide where ammonia and alcohol are removed by means
30 of the inert gas stream.

- The invention also provides a highly disperse hydrophobised silicon dioxide which can be obtained by the process according to the invention. This silicon dioxide is completely
35 free from the silanol groups normally present at the surface but carries at the surface a number of alkoxy or aryloxy groups corresponding to the number of free silanol groups on the surface of the silicon dioxide from
40 which it was prepared. As a result the silica is completely hydrophobic and lipophilic, i.e., it cannot be wetted in water at normal temperature, but at the same time shows proton affinity, i.e., it can be wetted with water after
45 prolonged boiling.

The process according to the invention is illustrated by the following Examples:

Example 1

- 50 a) Following activation by the method of British Patent Specification No. 1292328, 500 g of a pyrogenic silica (surface 120 m²/g BET, water content less than 1% by weight), were introduced into a vessel, placed under a vacuum, followed by the dropwise addition
55 over a few minutes at room temperature of 50 g (10% by weight) of tetra-*n*-butoxy silane. The vessel was vigorously shaken during this addition. After the vacuum had been eliminated with nitrogen, a dry NH₃ gas stream was
60 introduced into the product for a period of from 2 to 3 seconds. A sample taken 30 minutes after the ammonia had been passed through, remained completely unwettable with

water, even when intensively shaken. The aqueous phase was completely clear.

- b) The test described in Example 1a) was carried out in the same way, but without the NH₃-treatment.

A sample taken after 3 hours was substantially hydrophobic. After intensive shaking with water, the aqueous phase showed some signs of hazing.

A hydrophobic silica produced in accordance with Example 1a) was left standing over water at room temperature for 96 hours, being intensively shaken twice a day for a period of 5 minutes. At the end of the test the aqueous phase was still completely clear.

The reactivity of the same product completely hydrophobic at room temperature can be demonstrated by boiling with water by virtue of the proton affinity simultaneously present in it. After 30 minutes in water heated to 100°C, 20% of the originally hydrophobic silica had gone over into the aqueous phase.

Example 2

500 g of a mixed oxide (silica containing 1% by weight of Al₂O₃) with a BET-surface of 80 m²/g and a water content of less than 0.1% by weight, as confirmed by spectroscopy, were introduced into a vessel, placed under vacuum and sprayed with 50 g (10% by weight) of tetrakis-ethylhexoxy silane



for 3 minutes, during which the vessel was vigorously stirred. After the vacuum had been eliminated with nitrogen, a dry NH₃-gas stream was introduced into the mixture for 3 seconds. The product was then exposed for 1 hour to a temperature of 100°C in a rotary flask.

Thereafter, the product was completely hydrophobic. A sample was left standing over water at room temperature for 96 hours, being intensively shaken twice a day for a period of 5 minutes. The aqueous phase remained completely clear throughout.

Example 3

Following activation by the method of British Patent Specification No. 1337329, 500 g of a precipitated silica (BET surface 150 m²/g, water content less than 1% by weight) were sprayed at room temperature with 50 g (10% by weight) of tetra ethoxy silane, accompanied by intensive stirring.

After 5 minutes, a dry NH₃-gas stream was passed through the mixture while stirring for between 2 and 3 seconds.

15 minutes after the ammonia had been added, the product was no longer wetted by water.

Example 4

Following activation by the method of British Patent Specification No. 1292328, 500

g of a pyrogenic silica (BET surface 120 m²/g, water content less than 1% by weight) were introduced into a vessel and placed under vacuum, followed by the dropwise addition over a few minutes at room temperature of 75 g (15% by weight) of tetrabutyl orthotitanate (monomeric) preheated to approximately 70°C, accompanied by vigorous shaking.

After 30 minutes, the vacuum was eliminated with nitrogen and a dry NH₃-gas stream passed through the mixture for 2 to 3 seconds.

A sample was taken after 8 hours; it remained completely unwettable with water even after intensive shaking. The aqueous phase was still completely clear after standing for 8 days.

Our copending application 4538/74 (Serial No. 1371219) describes and claims a process for hydrophobising finely divided oxides of metals and/or silicon wherein the oxide particles are activated by treatment at a temperature of from 700 to 1000°C over a period of 60 seconds or less with a gas stream which is inert to the oxide in a fluidised bed or with a stream of a gas which is inert to the oxide flowing in countercurrent, the particles, completely freed from water, are then treated with an organo silicon compound, a stream of dry ammonia gas being allowed to act upon the oxide particles for a period of 60 seconds or less, before, during or after their treatment with the organo silicon compound.

WHAT WE CLAIM IS:—

1. A process for hydrophobising finely divided oxides of metals and/or of silicon by anchoring hydrocarbon radicals in firm chemical linkage to the oxide surface by intensively mixing with the oxide a hydrolysable metal or metalloid compound containing —OR groups, of the general formula



in which M represents an element of the IVth group of the Periodic System whilst each R represents an alkyl radical with 1 to 8 carbon atoms or an aryl radical, it being possible for the radicals R in the same molecule to be the same or different, or with an oligomer of such a compound, the oxide having a water content of less than 1% by weight.

2. A process as claimed in claim 1 wherein M is silicon or titanium.

3. A process as claimed in Claim 1 or 2 wherein the ester is allowed to act on the oxide by admixture at a pressure of from 1,000 Torr to 10⁻² Torr and at a temperature of from 20°C to 300°C over a period of from one minute to 24 hours.

4. A process as claimed in any of Claims 1 to 3, wherein the oxide used as a starting material has a water content of from 0.2% to 0%.

5. A process as claimed in any of Claims 1 to 3, wherein, after activation by treatment at a temperature of from 700 to 1,000°C for a period of less than 60 seconds with a gas stream inert to the oxide either in a fluidised bed or with a stream of the inert gas flowing in countercurrent, the oxide is treated with a tetra-alkoxy silane or with an oligomer thereof.

6. A process as claimed in any of Claims 1 to 4, wherein the oxide is treated with dry NH₃-gas before, during or after admixture of the oxide with the ester compound.

7. A process as claimed in any of Claims 1 to 6, wherein the oxide is admixed with the ester compound at a temperature of from 20 to 200°C.

8. A process as claimed in any of Claims 1 to 7, wherein the oxide is admixed with the ester compound at a temperature of from 20°C to 35°C.

9. A process for the preparation of hydrophobised finely divided oxides substantially as hereinbefore described with reference to any of Examples 1 to 4.

10. Hydrophobised finely divided oxides when prepared by a process as claimed in any of Claims 1 to 9.

11. A highly disperse hydrophobised silicon dioxide which is completely hydrophobic and lipophilic but at the same time shows proton affinity as herein defined, and which is completely free from silanol groups at the surface but carries at the surface a number of alkoxy or aryloxy groups corresponding to the number of free silanol groups on the surface of the silicon dioxide from which it was prepared.

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